

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-087122

(43)Date of publication of application : 28.03.2000

(51)Int.Cl.

B22F 9/24

B01J 13/00

H01B 1/22

H01B 5/14

(21)Application number : 10-259965

(71)Applicant : MITSUBISHI MATERIALS CORP

(22)Date of filing : 14.09.1998

(72)Inventor : OKA TOMOKO

HAYASHI TOSHIHARU

SHIBUTA DAISUKE

(54) DISPERSION OF FINE METAL PARTICLES AND ITS PREPARATION

(57)Abstract:

PROBLEM TO BE SOLVED: To prepare a dispersion of fine metal particles capable of forming a transparent electrically conductive film in which two or more metals are uniformly distributed over the entire film.

SOLUTION: An aq. soln. (A) contg. salts of one or more metals selected from the group consisting of Au, Pt, Ir, Pd, Ag, Rh, Ru, Os, Re and Cu is mixed with an aq. soln. (B) contg. citric ions and ferrous ions in an atmosphere not substantially contg. oxygen at 25-95°C under stirring to precipitate fine metal particles in the mixed soln. When two or more metals are precipitated, fine metal particles in which these metals are alloyed in the same particle are formed and every particle has the same metal compsn.

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] A manufacturing method of metal particulate dispersion liquid characterized by comprising the following.

Solution (A) containing a salt of one sort or two sorts or more of metal chosen from Au, Pt, Ir, Pd, Ag, Rh, Ru, Os, Re, and a group that consists of Cu(s). A process to prepare

Solution (B) containing a citrate ion and ferrous ion. It is (A) in a process to prepare and atmosphere which does not contain oxygen substantially. Liquid and (B) A process which mixes liquid and makes metal particles generate

[Claim 2] (A) Liquid and (B) A manufacturing method of the metal particulate dispersion liquid according to claim 1 which includes further a process of collecting and carrying out the demineralization step of the metal particles from mixed liquor, and a process of carrying out re dispersion of the metal particles by which the demineralization step was carried out to water and/or an organic solvent, after a process of mixing liquid.

[Claim 3] (B) A manufacturing method of the metal particulate dispersion liquid according to claim 1 or 2 which also performs a process of preparing liquid, in atmosphere which does not contain oxygen substantially.

[Claim 4] (A) Liquid and (B) A manufacturing method of metal particulate dispersion liquid given in any 1 paragraph of claims 1 thru/or 3 which perform under stirring a process of mixing liquid, at temperature of 25-95 °C.

[Claim 5] (B) Liquid is (A). A manufacturing method of metal particulate dispersion liquid given in any 1 paragraph of claims 1 thru/or 4 which contains a citrate ion and ferrous ion of quantity of a mol one to 5 times to the total valence number of a metal ion in liquid, respectively and which is pH three to 10 solution. [of a range]

[Claim 6] (A) Liquid and (B) The last pH after mixing with liquid is (A) so that 3-9, and a stoichiometrical metal generated amount may become within the limits of 2 - 60 g/L. Liquid and (B) A manufacturing method of metal particulate dispersion liquid given in any 1 paragraph of claims 1 thru/or 5 which prepares liquid.

[Claim 7] (A) Liquid and (B) About mixing with liquid, it is (B). It is (A) to liquid. A manufacturing method of metal particulate dispersion liquid given in any 1 paragraph of claims 1 thru/or 6 performed by adding liquid.

[Claim 8] (A) In liquid, Pd/(Pd+Ag) weight ratio is 0.001. A manufacturing method of metal particulate dispersion liquid given in any 1 paragraph of claims 1 thru/or 7 which contain Ag salt and Pd salt above in the range which becomes less than one.

[Claim 9]The pH of metal particulate dispersion liquid obtained after a demineralization step and re dispersion. In 3.2-8.0, and conductivity, a metal content. A manufacturing method of metal particulate dispersion liquid given in any 1 paragraph of claims 2 thru/or 8 which are within the limits which is 0.1 to 10 % of the weight. [below 2.0 mS/cm]

[Claim 10]It is the dispersion liquid which made water and/or an organic solvent distribute metal particles containing two or more sorts of metal chosen from Au, Pt, Ir, Pd, Ag, Rh, Ru, Os, Re, and a group that consists of Cu(s), When these dispersion liquid are centrifuged with different gravitational acceleration of two or more, a metal composition ratio is [in every gravitational acceleration] substantially the same at upper liquid and precipitate. (a difference is less than 6%) Metal particulate dispersion liquid which comes out and is characterized by a certain thing.

[Claim 11]Metal particles are the metal particulate dispersion liquid according to claim 10 containing Ag and Pd, and Pd/(Pd+Ag) weight ratio of particles 0.001 or more, less than 1, metal particulate dispersion liquid whose first [an average of] particle diameter is within the limits of 1 - 15 nm.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention is metal particulate dispersion liquid of the metal kind of the precious metals, copper, etc. (namely, metallic colloid) Metal particulate dispersion liquid which can be manufactured by the manufacturing method and this method (metallic colloid) It is related. Although the metal particulate dispersion liquid manufactured by the method of this invention is useful for various uses, It is suitable for formation of the transparent conducting film for giving static electricity antistatic property and electromagnetic wave shielding [including ultraviolet rays and infrared rays] to the cathode-ray tube or CRT tube of TV or a computer which especially needs low-temperature baking also in a transparent conducting film.

[0002]

[Description of the Prior Art]Since the particles (colloidal particle) of metal [particle diameter / first / an average of], such as several nanometers - tens of nm, can make light penetrate, they can combine this with a binder and can form a transparent conducting film. Especially, the particles of silver with high conductivity are often used for this use.

[0003]Since the dispersion liquid (metallic colloid) which made water distribute metal particles are lacking in the compatibility between the metal particles which are hydrophobic colloid and are dispersoids, and the water which is carrier fluid, it is thermodynamically unstable, and if an electrolyte exists, it will be easy to cause condensation. Then, it is necessary to add the protective colloid (hydrophilic colloid, such as a water soluble polymer) which has the operation which stabilizes hydrophobic colloid in large quantities, and to stabilize metallic colloid.

[0004]If metallic colloid contains a lot of protective colloid, when using this for formation of a transparent conducting film, protective colloid which is an organic matter without conductivity blocks conductivity. Therefore, elevated temperature (an example and more than 350 **) that an organic matter decomposes and disappears thoroughly the baking temperature at the time of transparent conducting film formation Sufficient conductivity cannot be obtained unless it carries out. However, when forming a transparent conducting film in the cathode-ray tube or CRT tube of TV or a computer, since omission of the fluorescent substance in a cathode-ray tube, the fall of dimensional accuracy, and the change of vacuum balance and the corrosion of an electron gun by the generation of gas take place, such a high baking temperature cannot be adopted, for example.

[0005]It is 100 to make the solution of metal salt react to a reducing agent, and to manufacture metallic

colloid. Although more than the year is known from before, Method which Carey Lea announced in 1889 (M. Carey Lea, American Journal of Science, 37:491, 1889) If it removes, all will use a lot of protective colloid for stabilization of metallic colloid.

[0006]The method of Carey Lea mixes sodium-acid-citrate solution and ferrous sulfate solution, Solution of the reducing agent containing a citrate ion and ferrous ion (namely, solution of ferrous sulfate) It is the method of obtaining silver colloid, by preparing, mixing the solution of this reducing agent with a silver nitrate aqueous solution, and returning silver nitrate. In order for a citrate ion to stabilize the colloid by which the silver particulate was adsorbed, even if it does not add protective colloid of polymers, silver colloid is held stably.

[0007]Theoretically, this method is applicable also to manufacture of colloid of other precious metals by using the solution of other precious-metals salts instead of a silver nitrate aqueous solution.

[0008]The silver colloid liquid based on the method of this Carey Lea and its manufacturing method are indicated by JP,10-66861,A. Mixing with the solution of the above-mentioned reducing agent and a silver nitrate aqueous solution is performed under stirring of 1000 - 10000 rpm, and the silver particulate from which temperature or agitating speed is preferably changed on the way, and a particle size differs is made to generate in this method. The silver particulates which deposited are collected by centrifugal separation, water is distributed so that silver solids concentration may be 1 to 80 % of the weight, and it uses as a coating material for transparent conducting film formation.

[0009]

[Problem(s) to be Solved by the Invention]The method indicated by the above-mentioned method and JP,10-66861,A of Carey Lea can obtain stable colloid about silver colloid or colloid of the precious metals of a certain kind.

[0010]However, about other metal called the other precious metals and copper, stable metallic colloid is not necessarily obtained by a described method. Two or more sorts of metal kinds (an example, silver, and palladium) When the used metallic colloid was manufactured with a described method, it became clear that there was a big problem.

[0011]Namely, metal of a different kind in a described method (for example, silver and palladium) The metallic colloid which deposited independently is obtained. Therefore, when this metallic colloid is used as a coating material, metal particles move during membrane formation or baking, the particles of the same metal kind gather easily, and there is a tendency which the film over which metal of a different kind was distributed unevenly generates. If it becomes so, membrane characteristics cannot change by a membranous part and cannot form the transparent conducting film of the stable quality.

[0012]The transparent conducting film which mixed with the binder the conventional silver colloid mentioned above, and formed membranes this invention persons, Heat resistance, moisture resistance, chemical resistance, weatherability (ultraviolet resistance) The said endurance is not necessarily enough, For example, long term deterioration was carried out on the cathode-ray tube etc., and membranous electrical resistance increased gradually, and there is a possibility that it may become impossible to achieve the characteristic required of a transparent conducting film, especially an electromagnetic wave shielding function, and also it knew that a film would exfoliate easily. And it found out that the endurance of the transparent conducting film formed from this silver colloid was remarkably improved by mixing of palladium, i.e., use of silver and metallic colloid containing the particles of palladium.

[0013]However, when membranes are formed using the silver manufactured with the above-mentioned

conventional method, and metallic colloid containing the particles of palladium. As stated above, the transparent conducting film in which a silver particulate and palladium particles were distributed unevenly cannot generate, and silver and the transparent conducting film in which palladium was distributed uniformly cannot be obtained.

[0014]Metallic colloid which can form the transparent conducting film in which those metal was uniformly distributed over the whole film when this invention forms the transparent conducting film containing two or more sorts of metal kinds from metallic colloid (namely, metal particulate dispersion liquid) Let it be a technical problem to provide the method of manufacturing.

[0015]

[Means for Solving the Problem]This invention persons based on a manufacturing method of silver colloid of Carey Lea, A result of having repeated research about manufacture of metallic colloid containing particles of two kinds of metal, If a reaction condition at the time of mixing solution of a reducing agent and solution of metal salt which should be returned influences a reaction result greatly and performs this mixing in atmosphere which does not contain oxygen like an inert gas atmosphere substantially, Two kinds of metal mixed and deposited. (that is, it alloyed) It found out that metallic colloid containing metal particles was obtained.

[0016]Since two kinds of metal is alloying and every particle has the same metal composition ratio, metal particles in metallic colloid obtained by this method can obtain certainly a transparent conducting film in which two kinds of metal was uniformly distributed by every membranous part, when membranes are formed using this metallic colloid. That two kinds of metal is alloying in metal particles of this metallic colloid has metal composition ratio substantially same at upper liquid and precipitate in every gravitational acceleration, when metallic colloid is centrifuged with different gravitational acceleration. (a difference is less than 6%) It comes out and is confirmed by a certain thing.

[0017]This method is applicable also to metallic colloid containing three or more kinds of metal kinds. Even when the number of metal kinds is one, they are all the precious-metals kinds. (that is) [Au and] It was stabilized, metallic colloid of Pt, Ir, Pd, Ag, Rh, Ru, Os, and Re and Cu could be manufactured, and it also became clear that an effect that metal particles which deposited are detailed and variation in the particle size is very small was acquired.

[0018]Solution (A) containing a salt of one sort or two sorts or more of metal chosen from a group which this invention consists of here from **Au, Pt, Ir, Pd, Ag, Rh, Ru, Os, Re, and Cu A process to prepare, ** Solution (B) containing a citrate ion and ferrous ion It is (A) in a process to prepare and atmosphere which does not contain oxygen in ** real target. Liquid and (B) Manufacturing method of metal particulate dispersion liquid including a process which mixes liquid and makes metal particles generate.

[0019]This method is (A) at process **. Liquid and (B) After mixing liquid, a process of collecting and carrying out the demineralization step of the metal particles from mixed liquor, and a process of carrying out re dispersion of the metal particles by which the demineralization step was carried out to water and/or an organic solvent may be included further. Process ** which prepares (B) liquid is also preferably performed in atmosphere which does not contain oxygen substantially, and it is (A). Liquid and (B) Mixing with liquid is performed under stirring at temperature of 25-95 **.

[0020]In another side, this invention Au, Pt, Ir, Pd, Ag, Rh, It is the dispersion liquid which made water and/or an organic solvent distribute metal particles containing two or more sorts of metal chosen from a group which

consists of Ru, Re, Os, and Cu, When these dispersion liquid are centrifuged with different gravitational acceleration of two or more, a metal composition ratio is [in every gravitational acceleration] substantially the same at upper liquid and precipitate. (a difference is less than 6%) It is metal particulate dispersion liquid which comes out and is characterized by a certain thing.

[0021]In metal particles, Pd/(Pd+Ag) weight ratio of particles especially a desirable thing including Ag and Pd with this metal particulate dispersion liquid 0.001 or more, less than 1, and the first [an average of] particle diameter are within the limits of 1 - 15 nm. A transparent conducting film formed using this Ag-Pd particulate dispersion liquid, Compared with a transparent conducting film in which metal consists only of Ag, it cannot break out easily that a transparent conducting film in which endurance, such as chemical resistance, heat resistance, moisture resistance, and weatherability, improved remarkably, for example, was formed on a cathode-ray tube of TV shows [good antistatic property or electromagnetic wave shielding] over a long period of time, and a film exfoliates, either.

[0022]

[Embodiment of the Invention]The method of this invention is based on the manufacturing method of the metallic colloid of Carey Lea mentioned above.

[0023]First, solution (A) (henceforth (A) liquid) containing the salt of one sort or two sorts or more of metal which was chosen from Au, Pt, Ir, Pd, Ag, Rh, Ru, Os, Re, and the group that consists of Cu(s) and which it is going to deposit as metallic colloid It prepares. It is preferred to use the water-soluble metal salt easily returned to metal with a reducing agent as metal salt. Although the kind of desirable metal salt changes also with metal kinds, generally a nitrate, nitrite salt, sulfate, a chloride, acetate, etc. are preferred.

[0024]Although the kinds of desirable metal salt which can be used are enumerated next, The :Au:aurous chloride which is not restricted to these, an auric chloride, chloroauric acid, Pt : The first platinum of chloridation, The first platinum ammonium of chloridation, Ir : Iridium trichloride, iridium tetrachloride, Iridium hexachloride ammonium, iridium hexachloride 3 potassium, acetic acid iridium, Pd : Palladium chloride, palladium tetrachloride ammonium, and palladium potassium hexachloride, Palladium acetate, a palladium nitrate, Ag : Silver nitrate, silver nitrite, silver chloride, Rh : Rhodium trichloride, rhodium hexachloride ammonium, and rhodium potassium hexachloride, Hexamine rhodium chloride, acetic acid rhodium, Ru : A nitroso ruthenium nitrate, Ruthenium chloride, ruthenium-chloride ammonium, ruthenium-chloride potassium, ruthenium-chloride sodium, an acetic-acid ruthenium, Os:osmium trichloride, osmic-acid hexachloride ammonium, Re:rhodium trichloride, rhodium pentachloride, Cu: Copper sulfate, a cupric nitrate.

[0025]Especially desirable metal salt is the combination of Pd salt and Ag salt, and is (A) in this case. As for liquid, Pd/(Pd+Ag) weight ratio is 0.001. It is preferred above to contain Ag salt and Pd salt in the range which becomes less than one. This weight ratio is within the limits of 0.15-0.6 more preferably. Still more desirable metal salt is the combination of Pd salt and Ag salt.

[0026]It is solution (B) (henceforth (B) liquid) of a reducing agent independently. It prepares. The solutions of this reducing agent is a citrate ion and ferrous ion. (namely, ferrous citrate) It is solution to contain. Although the ferrous citrate is obtained as a crystal of monohydrate, since water solubility is low, this crystal is unsuitable to preparation of solution. Therefore, as Carey Lea adopted, it is preferred to supply a citrate ion and ferrous ion from a respectively different compound. That is, a citrate ion supplies citrate and/or citrate to ferrous ion from ferrous salt.

[0027]As citrate suitable for preparing solution, sodium acid citrate, potassium citrate, and ammonium citrate

are mentioned, and ferrous sulfate, iron nitrate, ammonium iron sulfate, a ferrous oxalate, and iron acetate are mentioned as ferrous salt. However, citrate or ferrous salt other than these are also water solubility and acidity. (or basicity) It is usable if suitable.

[0028](B) containing a citrate ion and ferrous ion Liquid prepares the solution of at least one sort of citrate compounds chosen from citrate and citrate, and can prepare it by adding at least one sort of ferrous salt to this with a solid. Or it is (B), when ferrous salt also prepares solution and mixes this solution with the solution of a citrate compound. Liquid may be prepared.

[0029]This (B) Since liquid acts as a reducing agent, it is easy to oxidize. (A) (B) before mixing with liquid It is (B) in "the atmosphere which does not contain oxygen substantially" later mentioned about a mixing process in order to prevent oxidation of liquid. It is preferred to prepare liquid and to save in this atmosphere to a mixing process.

[0030](A) Liquid and (B) As for the quantity, concentration, and pH of liquid, it is preferred to fulfill the following conditions. (B) Each quantity of the citrate ion and ferrous ion in liquid is (A). It is the range of an one to 5 time mol to the total valence number of the metal ion in liquid. (B) The ranges of pH in liquid are 3-10. (A) In the last pH after mixing and making liquid and (B) liquid react, 3-9, and a stoichiometrical metal generated amount serve as the range of 2 - 60 g/L.

[0031](A) prepared as mentioned above Liquid and (B) It is (A) when liquid is mixed. Metal salt (metal ion) in liquid is (B). It is returned to metal with the reducing agent (ferrous ion) in liquid, and deposits in liquid as metal particles, and metal particulate dispersion liquid, i.e., metallic colloid, generates. In this invention, this mixing is performed in the atmosphere which does not contain oxygen substantially. Preferably, it is 25-95 ** in temperature about this mixing, and is (B) under stirring. It is (A) to liquid. It carries out by adding liquid.

[0032]This mixing has been conventionally performed in the air. In that case, when the metal kind deposited especially is two or more sorts, each metal kind deposits as separate particles. As a result, gravitational acceleration (an example, 500, 1000, 1500xG) of two or more which is different in the generated metal particulate dispersion liquid If upper liquid generally differs in the analytical value of a metal composition ratio from precipitate and gravitational acceleration moreover changes when it centrifuges, any analytical value of upper liquid and precipitate will be changed. Therefore, when, separating the metal particles which deposited by centrifugal separation for example, it is dramatically difficult to change the metal composition ratio of the metal particles which prediction of the metal composition ratio of the separated metal particles became difficult, and were separated by slight change of centrifugal separation conditions, and to obtain the metal particles of the fixed quality.

[0033]When the dispersion liquid containing the metal particles to which the metal kind of a different kind deposited independently are used as a coating material, metal particles move during membrane formation or baking, the particles of the same metal kind gather easily, and there is a tendency which the film over which each metal was distributed unevenly generates. If it becomes so, membrane characteristics cannot change by a membranous part and cannot form the transparent conducting film of the stable quality. The metal particles deposited in the atmosphere have a bad dispersion state because of being easy to produce an oxide and particle size distribution becoming uneven etc. As a result, the problem that it is bad and a film becomes uneven also has the preservation stability of liquid.

[0034]According to this invention, it is (A) under stirring at the temperature of 25-95 ** preferably among the atmosphere which does not contain oxygen substantially. Liquid and (B) If it mixes with liquid, When a metal

[0035]therefore, since a metal composition ratio is hardly changed even if the metal composition ratio of the metal particles separated even if it separated the metal particles which deposited by centrifugal separation is substantially [as the metal composition ratio in liquid] the same and it changes centrifugal separation conditions sharply, a metal composition ratio can always obtain the metal particles of about 1 law. When the obtained metal particulate dispersion liquid is used as a coating material, even if metal particles move during membrane formation or baking, since the metal composition ratio is the same, the metal composition ratio can form the transparent conducting film of the stable quality in which it did not change but each metal was always distributed uniformly by all the particles.

[0037](A) Liquid and (B) As for "the atmosphere which does not contain oxygen substantially" at the time of mixing of liquid, oxygen tension means the atmosphere below 0.05 atm. When mixing by a sealing system, a vacuum or an inert gas atmosphere can attain this atmosphere. However, since mixing is generally performed by a open system, the above-mentioned atmosphere is inactive gas. (an example, nitrogen, argon, helium) What is necessary is just to attain by making it circulate. When economical efficiency is taken into consideration, mixing under nitrogen circulation is preferred. Although reducing gas called the mixed gas of hydrogen, hydrogen, and inactive gas can also be used, since it is an inflammability, inactive gas is easier for handling.

[0039]It is preferred to perform mixing under stirring. Although agitating speed in particular is not restricted, probably, it is usually within the limits of 30 - 1000 rpm. What is necessary is just to determine agitating speed and temperature that a desired particle size and composition ratio are obtained, since agitating speed and the temperature at the time of mixing influence the particle size of the metal particles which deposit and temperature also influences the metal composition ratio of the metal particles which consist of two or more sorts of metal kinds.

[0040] Mixing time is chosen so that reduction of metal salt may be completed nearly thoroughly. Usual is 5-120. A between [parts] grade may be sufficient. In this way, the obtained metal particulate dispersion liquid is

the concentration adjustment of remaining as it is or metal particles. (dilution or concentration) It only carried out and is a suitable use. (preparation of an example and a coating material) It can also be used. However, in liquid, a lot of electrolytes as an unreacted material or a resultant exist, and this is a product. (an example, a transparent conducting film) Quality is worsened in many cases.

[0041] Therefore, metal particles are collected from the dispersion liquid obtained by mixing, the electrolyte which performed the suitable demineralization step and adhered is removed, and it is re dispersion to water and/or an organic solvent. (repulping) Carrying out is preferred. What is necessary is just to perform it by suitable methods, such as sedimentation, filtration, and centrifugal separation, although recovery of metal particles is based also on the state of aggregation. Ionic exchange or dialysis can perform a subsequent demineralization step, for example. The method of making the particles which add sodium nitrate solution and are distributed condensing, and flushing and centrifuging them may be used. In such a demineralization step, the citrate ion by which metal particles are adsorbed is not removed, but plays the role like protective colloid which this citrate ion makes stabilize distribution of metal particles.

[0042] It is water so that it may become a desired metal content at the metal particles which carried out the demineralization step. (deionized water) And/or, water miscible organic solvents (an example, alcohol, ketone, alkoxy alcohol, etc.) are added, re dispersion of the metal particles is carried out, and metal particulate dispersion liquid is obtained again. The metal particulate dispersion liquid of this invention can also be thoroughly used as the dispersion liquid of a non-drainage system, if a suitable dispersing agent (an example, a surface-active agent) is added. For example, what is necessary is to collect metal particles from the dispersion liquid which carried out the demineralization step, and just to carry out re dispersion to the organic solvent containing a suitable additive agent. That is, carrier fluid in the metal particulate dispersion liquid of this invention can also be considered as the mixed solvent of water, water, and an organic solvent and an organic solvent, and ***** Paint additive agents, such as a pH adjuster, and a modifier may be added if needed.

[0043] In this way, pH metal particulate dispersion liquid after carrying out a demineralization step In 3.2-8.0, and conductivity, a metal content. It is preferred that it is within the limits which is 0.1 to 10 % of the weight. [below 2.0 mS/cm] On condition of besides this range, a dispersion state may become unstable. The citrate ion is sticking to metal particles on the surface, and this stabilizes a dispersion state like protective colloid.

[0044] With a described method, Au, Pt, Ir, Pd, Ag, Rh, Ru, Os, It is dispersion liquid of the metal particles containing two or more sorts of metal chosen from the group which consists of Re and Cu, When these dispersion liquid are centrifuged with different gravitational acceleration of two or more, a metal composition ratio is [in every gravitational acceleration] substantially the same at upper liquid and precipitate. (a difference is less than 6%) The metal particulate dispersion liquid which comes out and is characterized by a certain thing is obtained.

[0045] In this way, one especially desirable in the metal particulate dispersion liquid obtained contains the metal particles which Ag and Pd alloyed, and Pd/(Pd+Ag) weight ratio of particles are 0.001. Less than 1 and the first [an average of] particle diameter are within the limits of 1 - 15 nm above. More desirable Pd/(Pd+Ag) weight ratio are 0.15-0.6.

[0046] This Pd or Pd/Ag particulate dispersion liquid is dramatically suitable for forming a transparent conducting film in the cathode-ray tube of TV or a computer, It compares with the transparent conducting film which consists of Ag particulates, and they are heat resistance, moisture resistance, chemical resistance, and

weatherability. (ultraviolet resistance) The said endurance can form the dramatically outstanding transparent conducting film.

[0047]In order to form a transparent conducting film from this metal particulate dispersion liquid, it is a suitable binder for these dispersion liquid. (an example, aqueous organic resin) Although it mixes directly and the method of applying to a base with a suitable cathode-ray tube etc. can also be adopted, A desirable method is spreading (overcoat) about a binder solution suitable from it after applying this metal particulate dispersion liquid to a base as it is, making it dry and forming on a base the film which consists only of metal particles. It is the method of carrying out. Since the remaining binder solutions that were not able to permeate form the upper coating which does not contain metal particles, a two-layer film called lower layer metal particle membranes and the upper tapetum lucidum is formed, at the same time a binder solution permeates all over the opening of lower layer metal particle membranes and it combines metal particles.

[0048]As a binder used for overcoat, Polyester resin, an acrylic resin, an epoxy resin, melamine resin, urethane resin, A metal alkoxide or its hydrolyzates, such as organic system binders, such as butyral resin and ultraviolet curing nature resin, and silicon, titanium, and a zirconium (an example, silica sol) All of inorganic system binders, such as a silicone monomer and a silicone oligomer, can be used.

[0049]As for a binder, what can form the tapetum lucidum whose refractive index is smaller than lower layer metal particle membranes is preferred. Thereby, a two-layer film becomes low reflection nature, and, in addition to antistatic property and electromagnetic wave shielding, anti-dazzle property can also be given to a base. Silica precursor in which especially the desirable binder can form the nature tunic of silica (an example, alkoxysilane, and its hydrolyzate, silica for example, sol) It is.

[0050]

[Example]The metal salt chosen from the following was dissolved in deionized water, and the metallic salt solution was prepared for every metal. Au: -- chloroauric acid, the first platinum of Pt:chloridation, Ir:iridium trichloride, Pd:palladium nitrate, Ag:silver nitrate, and Rh: -- rhodium potassium hexachloride, Ru:ruthenium trichloride, Os:osmium trichloride, Re:rhenium trichloride, and Cu:copper sulfate.

[0051]Direct, in addition the reducing agent solution which makes it dissolve and contains a citrate ion and ferrous ion by the mole ratio 3:2 were prepared for granular ferrous sulfate in the nitrogen gas air current at the temperature shown in the 26% sodium-acid-citrate solution which obtained sodium acid citrate by making it dissolve in deionized water independently in Table 1.

[0052]Stirring either of the obtained reducing agent solution at 100 rpm with a nitrogen gas air current and temperature held, any one sort of the above-mentioned metallic salt solution or two sorts were dropped at this solution, and it mixed. The mixture ratio which showed these in Tables 1 and 2 when two kinds of metallic salt solutions were added (% of the weight) It mixed beforehand at a rate which becomes, the mixed metal salt water solution containing two kinds of metal salt was prepared, and this mixed metal salt water solution was added in reducing agent solution. Even if in any case the metallic salt solution of the room temperature was dropped by adjusting the concentration of each solution so that the quantity of a metallic salt solution might become 1/10 or less [of the quantity of reducing agent solution], reaction temperature was held at prescribed temperature.

[0053]As for the mixture ratio of both solution, the mole ratios of the citrate ion and ferrous ion in reducing agent solution to the total valence number of the metal ion in a metallic salt solution are all. It was made to become a mol 0.5 to 6 times. After the end of dropping of a metallic salt solution, stirring was continued for 15

more minutes and metal particulate dispersion liquid was obtained. The pH of these dispersion liquid was within the limits of 3-9, and the stoichiometrical metal generated amount was within the limits of 2 - 60 g/L. [0054]deionized water after allowing the obtained dispersion liquid to stand at a room temperature, and a decantation separates the metal particles which sedimented, and boiling separated substances, adding deionized water, considering it as a dispersing element and carrying out a demineralization step by dialysis -- in addition, the metal content used the metal particulate dispersion liquid of 4.0 weight %. pH these dispersion liquid Within the limits of 3.2-8.0 was 2 or less mS/cm in conductivity. The mean particle diameter of the metal particles in dispersion liquid was measured from survey of 100 particles with the TEM photograph. Although particle size distribution was not measured, also when it was any, particle diameter was dramatically uniform and not less than 90% of particles had less than **20% of particle diameter of mean particle diameter. [0055]ICP (inductive-coupling high frequency plasma) of a sample which extracted it in this way after stirring well the metal composition ratio of a demineralization step and the whole metal particulate dispersion liquid after carrying out re dispersion when metal particles contained two or more sorts of metal It asked by the spectroscopic analysis. It is electrolyte addition by a case in a part of these dispersion liquid. (30wt% sodium nitrate solution is added in 0.2 wt% of quantity to colloid weight) After carrying out, The metal composition ratio in each of the upper liquid obtained by centrifuging for 5 minutes with the gravitational acceleration shown in Table 1 and a precipitating part was similarly analyzed as the above. These results were also shown in Table 1.

[0056]The result at the time of preparing the metal particulate dispersion liquid containing Ag and Pd like the above was also written together to Table 1 except having performed each of preparation of reducing agent solution and mixing with a metallic salt solution and reducing agent solution in the air for comparison.

[0057]

[Table 1-1]

試 驗 No	金屬鹽	金屬組成重量比		混合・反應條件			微粒子 分散液 特性	濾心分離原理試驗結果			備考			
		混合比	分散液中	雰囲気	溫度 (℃)	pH		化學濃度的 生成量 (g/L)	電解質 添加	條件 × C		金屬組成重量比 上液	沈殿	
1	Ag/Pd	95/4	95.8/4.2	窒素	60	5.0	15	5	5.6	なし	1000	95.7/4.3	95.5/4.5	
2											1500	95.5/4.5	96.0/4.0	
3		90/10	90.3/9.7	窒素	42	5.0	40	10	5.4	なし	1500	90.0/10.0	90.2/9.8	
4		80/20	81.0/19.0	窒素	41	5.0	20	8	5.1	なし	1000	80.2/19.8	81.0/19.0	
5											1500	81.1/18.9	80.2/20.3	
6			80.5/19.5		59	5.0	20	10	4.7	なし	1000	81.1/18.9	80.1/19.9	
7											1500	80.8/19.2	79.8/20.2	
8		75/25	75.8/24.2	窒素	25	5.0	5	4	5.8	なし	1500	75.8/24.2	75.3/24.7	
9		70/30	70.9/29.1	窒素	95	5.0	30	10	3.5	なし	1500	71.0/29.0	69.8/30.2	
10		60/40	60.8/39.2	窒素	40	5.0	10	5	4.6	なし	1500	60.9/39.1	59.8/40.2	
11		50/50	56.5/43.5	窒素	42	5.5	20	5	5.0	なし	500	56.6/43.4	55.3/44.7	
12											1000	56.4/43.6	57.4/42.6	
13											1500	55.9/44.1	55.2/44.8	
14										30wt% NaNO ₃	500	55.6/44.4	55.3/44.7	
15											1000	56.2/43.8	56.0/44.0	
16											1500	56.1/43.1	55.9/44.1	
17		53.6/46.4	窒素		60	5.5	20	6	4.8	なし	1500	52.5/46.5	52.3/47.7	
18		43.9/56.1	窒素		79	5.5	20	6	4.7	なし	1500	43.5/56.5	44.0/56.0	
19		61.6/38.4	空気		40	5.5	20	12	4.8	なし	500	62.4/37.6	59.8/40.2	比較例
20											1000	67.0/33.0	56.0/45.0	比較例
21											1500	73.5/26.5	47.1/52.9	比較例
22											500	—	—	比較例
23											1000	—	—	比較例
24											1500	—	—	比較例
25		40/60	39.2/60.8	窒素	40	5.5	20	8	5.0	なし	1500	39.5/60.5	38.8/61.2	
26		30/70	28.5/72.5	窒素	45	5.5	15	10	5.2	なし	1500	29.0/71.0	28.4/71.6	
27		99.9/0.1	99.1/0.1	窒素	30	5.5	20	10	4.8	なし	1500	99.9/0.1	99.9/0.1	

[0058]

[Table 1-2]

試 驗 No	金屬種	金屬組成重量比		混合・反應條件			微粒分散液特性		溶解質添加		條件	金屬組成重量比		備考
		混合比	分散液中	霧狀	溫度 (°C)	pH	化學實驗的 生成量 (g/L)	粒径 (nm)	pH		× G	上 液	沈 澱	
28	Pd/Au	50/50	49.0/51.0	窒素	60	5.8	2	11	5.8	なし	1500	48.2/51.8	49.5/50.5	
29	Pt/Au	50/50	45.0/55.0	窒素	55	6.0	5	12	5.5	なし	1500	46.1/53.9	44.9/55.1	
30	Ag/Au	80/20	78.5/21.5	窒素	53	5.5	5	6	5.4	なし	1500	78.8/21.2	79.0/21.0	
31	Ag/Ru	80/20	79.0/21.0	窒素	67	4.9	5	7	4.8	なし	1500	79.7/20.3	78.5/21.5	
32	Ag/Cu	50/50	46.9/53.1	窒素	55	5.6	5	7	5.0	なし	1500	47.4/52.6	46.5/53.5	
33	Pd/Pt	80/20	81.9/18.1	窒素	55	6.1	5	6	4.0	なし	1500	80.4/19.6	78.8/21.2	
34	Pd/Cu	50/50	46.8/53.2	窒素	60	6.3	5	8	4.8	なし	1500	47.5/52.5	48.0/52.0	
35	Pt	—	—	窒素	50	6.0	10	3	4.5	—	—	—	—	
36	Au	—	—	窒素	60	5.4	5	4	4.7	—	—	—	—	
37	Ir	—	—	窒素	40	5.6	5	4	4.4	—	—	—	—	
38	Ag	—	—	窒素	30	5.8	15	6	5.5	—	—	—	—	
39	—	—	—	窒素	30	5.4	15	25	5.1	—	—	—	—	比較例
40	Pd	—	—	窒素	60	5.6	10	8	5.4	—	—	—	—	
41	—	—	—	窒素	60	5.5	10	28	4.5	—	—	—	—	比較例
42	Rh	—	—	窒素	40	6.1	5	6	4.7	—	—	—	—	
43	Ru	—	—	窒素	35	5.4	5	8	5.6	—	—	—	—	
44	Os	—	—	窒素	40	5.7	10	4	4.8	—	—	—	—	
45	Cu	—	—	窒素	46	5.3	5	9	4.9	—	—	—	—	
46	Re	—	—	窒素	38	5.5	5	5	5.2	—	—	—	—	

[0059]As shown in Table 1, mean particle diameter can obtain the quality metal particulate dispersion liquid to which the particle size was well equal by several nanometers - tens of nm about every metal kind by the method of this invention. On the other hand, in the comparative example made to mix and react in the air, even if it was which [of Ag-Pd Ag, and Pd] case, the mean particle diameter of metal particles became much larger.

[0060]especially -- it should observe -- it is dispersion liquid of metal particles including two or more sorts of metal kinds. By the comparative example performed in the air like before, mixing with a metallic salt solution

and reducing agent solution.500 When it centrifuged by 1000 and 1500xG, and upper liquid differed in the analytical value of the metal composition ratio greatly from precipitate and gravitational acceleration moreover changed with any gravitational acceleration, any analytical value of upper liquid and precipitate was changed. For example, in the Ag/Pd system shown in Table 1-1, when the metal composition ratio of the upper liquid in the same gravitational acceleration and precipitate was compared with any gravitational acceleration, many Ag in upper liquid was contained and many Pd to precipitate was contained. The rate of Ag increased with upper liquid and the rate of Pd increased in precipitate, so that gravitational acceleration became high. Since this means that Ag and Pd deposit independently and differs in the surface state and oxidation state of an Ag particle and Pd particles, it is considered that centrifugal separation showed such an action. Anyway, if the metal composition ratio in precipitate differs from dispersion liquid and centrifugal separation conditions change, each of upper liquid and metal composition ratios of precipitate will be changed.

[0061]Thus, if a metal kind of a different kind deposits independently, when this metal particulate dispersion liquid is used as a coating material, metal particles move, the particles of the same metal kind cannot gather easily, the film over which each metal was distributed unevenly cannot generate, and uniform and stabilized membrane characteristics cannot be acquired.

[0062]On the other hand, in the example of this invention which performed mixing with a metallic salt solution and reducing agent solution in the nitrogen air current according to this invention. 500 When it centrifuged by 1000 and 1500xG, even if the analytical value of a metal composition ratio is almost the same at upper liquid and precipitate and it changed gravitational acceleration with any gravitational acceleration, change of this metal composition ratio was dramatically small. This metal composition ratio was almost the same as the metal composition ratio in the mixed metal salt water solution used for reduction. Each of each metal particles is alloying this.

It means that metal composition is homogeneous.

Therefore, the film over which each metal was distributed homogeneously is always obtained, and uniform and stabilized membrane characteristics can be acquired.

[0063]

[Effect of the Invention]According to this invention, the mean particle diameter which consists of one sort chosen from Au, Pt, Ir, Pd, Ag, Rh, Ru, Os, Re, and the group that consists of Cu(s), or two sorts or more is as detailed as several nanometers - tens of nm, Metal dispersion liquid to which the particle size was well equal and which quality metal particles distributed (metallic colloid) It can stabilize and manufacture.

[0064]Especially about the dispersion liquid of metal particles including two or more sorts of metal kinds. Since component metals are alloyed and contained in metal particles and all the particles have the almost same metal composition ratio, the transparent conducting film in which the metal distribution in a film has the uniform always and stabilized quality can be formed using this metal particulate dispersion liquid.

[Translation done.]